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Comparative organic geochemistry of Indian margin (Arabian Sea) sediments: estuary to continental slope

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Abstract. Surface sediments from sites across the Indian margin of the Arabian Sea were analysed for their elemental and stable isotopic organic carbon (C_{org}) and total nitrogen compositions, grain size distributions and biochemical indices of organic matter (OM) source and/or degradation state. Site locations ranged from the estuaries of the Mandovi and Zuari rivers to depths of ∼ 2000 m on the continental slope, thus spanning nearshore muds and sands on the shelf and both the oxygen minimum zone (OMZ) on the upper slope (∼ 200–1300 m) and the seasonal hypoxic zone that appears on the shelf. Source indices showed mixed marine and terrigenous OM within the estuaries, but consistent predominance (80–100 %) of marine OM on the shelf and slope. Thus, riverine terrigenous OM is diluted or replaced by autochthonous marine OM and/or is efficiently re-mineralised, within or immediately offshore of the estuaries. Organic C contents of surface shelf sediments varied from < 0.5 wt % in relict shelf sands to up to ∼ 4 wt % for nearshore muds, while upper slope sites within the OMZ showed a wide range (∼ 2 to 7 + wt %), progressively decreasing below the OMZ to ≤ 1 wt % at 2000 m. Thus, major variability (∼ 5 wt %) was found at slope sites within the OMZ of similar depth and near-identical bottom-water O_2 concentrations. A strong relationship between $\%C_{org}$ and sediment grain size was seen for sediments within the OMZ, but lower relative C_{org} contents were found for sites on the shelf and below the OMZ. Further, C_{org} loadings, when related to estimated sediment surface area, indicated distinct enrichment of C_{org} in the OMZ sediments relative to sites above and below the OMZ and to sediments from normoxic margins. Diagenetic indices confirmed that lower C_{org} content below the OMZ is associated with more extensive OM degradation, but that shelf sediment OM is not consistently more degraded than that found within the OMZ. Together, the results indicate that OM distribution across the margin is controlled by interplay between hydrodynamic processes and varying preservation associated with O_2 availability. This inference is supported by multiple regression analysis. Hydrodynamic processes (expressed as %Silt) followed by O_2 availability, can explain the large majority of $\%C_{org}$ variability when the shelf and slope are considered as a whole. However, while O_2 becomes the primary influence on $\%C_{org}$ for sediments below the OMZ, %Silt is the primary influence across the OMZ and, apparently, the shelf. Thus, reduced O_2 exposure is responsible for OM enrichment within the OMZ, but hydrodynamic processes are the overriding control on sediment OM distributions across both the shelf and the OMZ.

1 Introduction

The Arabian Sea is exceptional both for monsoons that drive intense, seasonally variable productivity, and for its mid-depth oxygen minimum zone (OMZ, ∼ 200–1300 m). The ring of organic-matter-rich sediments that lines the Arabian Sea's margins coincides roughly with the OMZ, a feature that

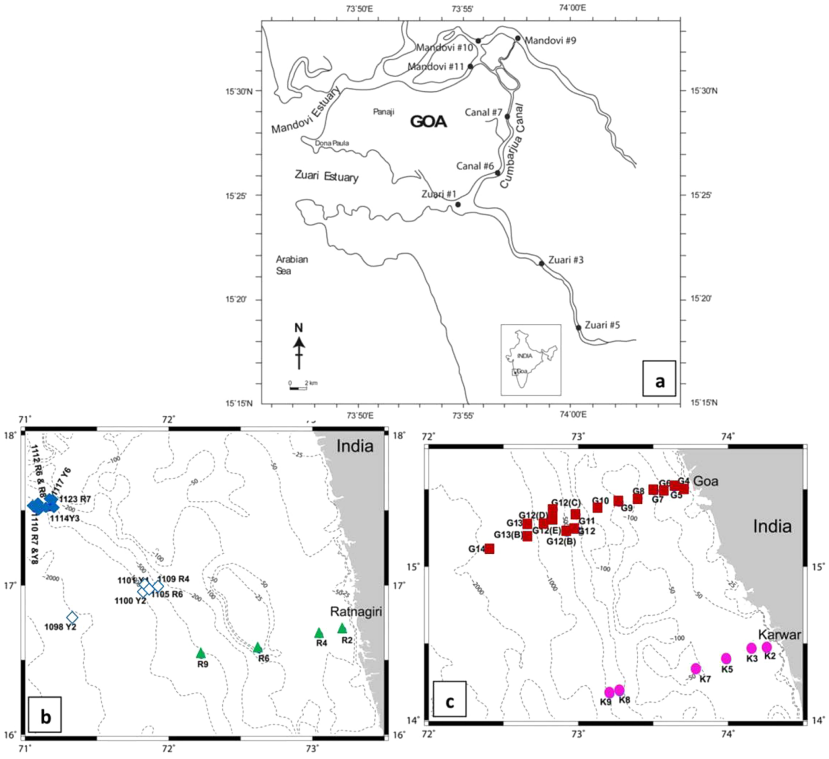

Figure 1. Sediment sampling locations; **(a)** within the Mandovi–Zuari estuary confluence (insert shows location relative to the Indian subcontinent as a whole), **(b)** Yokosuka (north and south) and Ratnagiri transects, **(c)** Goa and Karwar transects. Locations of panels **(b)** and **(c)** are immediately north and south of the Mandovi–Zuari confluence shown in panel **(a)** , respectively. Station labels are as defined in the legend to Fig. 4.

led O_2 availability to be proposed as a primary control on sediment organic matter (OM) distributions (e.g. Paropkari et al., 1992, 1993; van der Weijden et al., 1998; Keil and Cowie, 1999), and the Arabian Sea OMZ to be suggested as the modern equivalent of settings with OM-rich deposits found in the geological record (Demaison and Moore, 1980).

However, margins of the Arabian Sea differ markedly in productivity, and OMZ sediments experience differing degrees of O_2 depletion and thus have different benthic communities and degrees of bioturbation (Cowie, 2005). There is also variability in the magnitude and location (depth range) of sediment organic C maxima. Moreover, there is often a mismatch in the depths of organic C maxima and O_2 minima, and major variability in organic C content can occur without parallel variability in O_2 (e.g. Pedersen et al., 1992; Calvert et al., 1995; Cowie et al., 1999, 2009). This and other evidence has led to multiple other (interrelated) factors, including productivity, winnowing and cross-margin sediment transport, bottom topography and OM–mineral interactions to be invoked as contributing controls. The interactions and relative importance of these factors remain the subject of considerable research and debate (Cowie 2005, and references therein).

A further potential influence on margin sediment OM content and composition is OM source. A notable feature of the Arabian Sea is that sediments from all margins have generally been shown to contain OM that is overwhelmingly of marine origin, often even in nearshore shelf deposits. This is not surprising for the western margins (e.g. Smallwood and Wolff, 2000), where there are no major rivers depositing sediments. However, on the basis of stable isotopic, biomarker and petrographic evidence, it also appears to be true of the Pakistan margin, directly offshore of the Indus River (e.g. Cowie et al., 1999; Schulte et al., 2000; Jeffreys et al., 2009) and for the Indian margin (e.g. Calvert et al., 1995; Agnihotri et al., 2008; Kurian et al., 2013). The damming of the Indus in the 1970s dramatically reduced sediment export (e.g. Syvitski and Milliman, 2007), which might explain the present-day paucity of terrigenous OM in offshore sediments. However, the same marine predominance is also found throughout Holocene sediment records from the Pakistan margin (e.g. Schubert et al., 1998). For the Indian margin, the lack of a clear terrigenous OM signature in shelf and slope sediments is perhaps surprising given that rivers on this coast have particularly large runoff during the SW monsoons. The fate of the suspended sediments from these rivers, and if/how they contribute to shelf and slope OM deposits, remain unclear.

The Indian margin is also of particular interest because, in addition to the mid-depth OMZ that impinges on the upper slope, a belt of intense O_2 depletion develops from south to north along the entire western Indian shelf during the summer monsoons, usually peaking in September–October (Naqvi et al., 2000, 2006, 2009). This represents the largest coastal hypoxic zone on Earth, and, as a result of seasonal fluctuations in redox conditions (and therefore benthic communities), together with sediment bioturbation and ventilation, a further potential influence on shelf sediment OM content and composition.

However, previous assessments of sediment OM distributions on the Indian margin have lacked either comprehensive cross-margin sampling or systematic determination of parameters necessary to delineate OM source and degradation state, as well as content. We present here results from a range of analyses of sediments from transects spanning the western Indian margin, from estuaries to the continental shelf and across the upper slope, spanning both the seasonal coastal hypoxic zone and the semi-permanent OMZ on the continental slope. The broader objective was to elucidate the interactions and relative importance of factors including source, hydrodynamic processes and O_2 availability as OM distributional controls.

2 Methods

2.1 Setting, sampling locations and methods

Sediment samples were collected at sites across the upper Indian continental margin, from various points within the estuary confluence of the Mandovi and Zuari rivers (Fig. 1a) and across transects spanning the shelf and/or upper slope (to ∼ 2000 m depth) (Fig. 1b and c). Station details are presented in Table 1. Firstly, push cores (8.5 cm i.d.) were collected with the manned submersible *Shinkai 6500* on RV *Yokosuka* cruise YK0811 in 2008, at stations (500–2000 m depth) forming two transects (Yokosuka N and Yokosuka S) to the north of the Mandovi/Zuari estuary (Fig. 1b). Secondly, shelf sediments were collected on RV *Sindhu Sankalp* cruises in October 2010 and May 2011 (Fig. 1b and c). These were collected over three transects: offshore of the Mandovi/Zuari estuary confluence (Goa transect) and to the north (Ratnagiri transect, ∼ 16.5° N, S. Maharashtra) and south (Karwar transect, ∼ 16.4° N, N. Karnataka). The Goa transect also extended to a depth of 2056 m, thus fully spanning both the shelf and the permanent OMZ on the upper slope. Sediments were collected either by box core or grab, which were subsequently sub-cored with 8.5 cm i.d. plastic barrels. Finally, sediments from the Mandovi/Zuari estuary were collected by grab on a small coastal vessel. Sediment cores from selected stations were vertically sectioned at 1 cm intervals, and sediments were then freeze-dried, with weights being determined before and after drying.

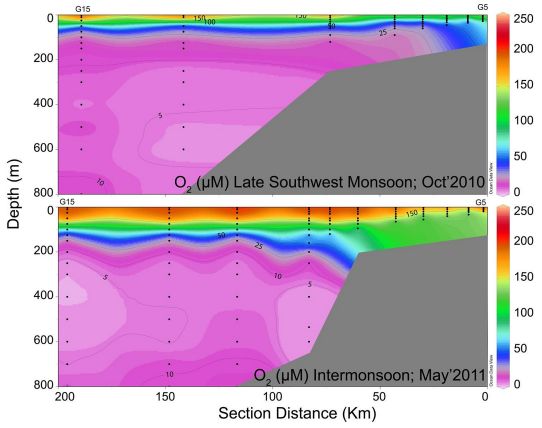

Figure 2. Cross-margin plots (to 800 m) of dissolved oxygen concentration (μM) during the late monsoon season (October 2010, upper panel) and intermonsoon season (May 2011, lower panel).

Together, these sites span an estuarine gradient (river to mouth) as well as the continental shelf and upper continental slope. Notably, the margin transect includes stations above, within and below the mid-water OMZ (dissolved oxygen (DO) ≤ 50 μM as defined by Helly and Levin (2004), ∼ 250–∼ 1300 m). As we note in the Discussion, a depth boundary of 1000 m is used for distinguishing sites within and below the OMZ, as a distinct change in DO values is seen at roughly this depth. The shelf sites span the full depth range (∼ 20 m to shelf break [∼ 200 m]), and experience extreme seasonal variability in bottom-water DO concentrations, from fully oxygenated during intermonsoon months to extreme hypoxia during the summer southwest monsoon (Fig. 2). The shelf-to-slope transects also span a wide range of sediment types, from fine muds nearshore and beyond the shelf break, to mid-shelf relict carbonate sands (Ramaswamy and Nair, 1989; Rao and Rao, 1995; see below).

Finally, suspended sediment samples from both rivers were collected with large-volume bottle sampling at sites upstream of the furthest inland seawater incursion, in October 2010 and May 2011. The samples were filtered onto pre-weighed glass fibre filters (0.7 μm nominal pore size).

2.2 Analytical

Sediments were analysed for their organic C (C_{org}) and total N (TN) contents and stable C and N isotopic compositions using CE Instruments NA2500 elemental analyser connected to a VG Isogas Prism III isotope ratio mass spectrometer. Freeze-dried sediments were decalcified by vapour-phase HCl acidification (Hedges and Stern, 1984) followed by the addition of 2–3 drops of purified 6 N HCl. Acetanilide was used as the calibration standard for elemental data, while $\delta^{15}N$ and $\delta^{13}C$ were respectively determined relative to air and the PACS-2 reference standard from the National Research Council Canada ($\delta^{13}C_{org} = -2.228$ ‰). Replicate

analyses of selected samples ($n = 2$–5) produced precision (% standard deviation; %sd) of < 2 and < 3.3 % for $\%C_{org}$ and %TN, respectively, and standard deviations of < 0.12 ‰ for $\delta^{13}C$ and 0.16 ‰ for $\delta^{15}N$. Grain size analyses were conducted by laser diffractometry on slurries of sediments disaggregated in an aqueous solution of sodium hexametaphosphate. Amino acids were determined by the method of Cowie and Hedges (1992a), which involved reverse-phase HPLC of 6 N HCl hydrolysates and fluorometric detection of orthophthaldialdehyde derivatives. Quantification was relative to charge-matched internal standards added after hydrolysis. Replicate analyses of selected samples ($n = 2$–3) produced a %sd of < 7 % of the mean for all amino acid parameters other than trace component yields and mole percentages (≤ 12 %). Lignin phenols were analysed by the method of Ertel and Hedges (1982) as modified by Goni and Montgomery (2000) and involved gas chromatographic separation and flame-ionisation detection of phenols liberated by alkaline CuO hydrolysis, quantified relative to internal standards added immediately post-hydrolysis. Precision (%sd) for individual phenols in replicate analyses of selected samples ($n = 2$–3) was < 10 % of mean values in most estuary and shelf samples, but was poorer for slope sites where phenol levels were close to detection limits. Precision for total phenol yields was < 20 % in all cases. All concentrations were corrected for sediment salt content, which were determined either by combining porewater contents with bottom-water salinities or by silver nitrate titration of dried sediment suspensions in distilled water.

3 Results and discussion

Station details, including locations, depths and bottom-water DO concentration (at the time of sampling) are recorded in Table 1, alongside results of all elemental, stable isotopic, biochemical and grain size analyses.

3.1 Cross-margin organic matter distributions

Sediment organic C concentrations ($\%C_{org}$, wt %) range from ∼ 0.2 % in selected estuary and mid-shelf deposits (all coarser sediments, see below) to a maximum of ∼ 7 % at upper slope sites (∼ 500–800 m) (Fig. 3). Below the lower boundary of the permanent mid-water OMZ there is a progressive drop, reaching ∼ 1–1.5 wt % at ∼ 2000 m. While maximal $\%C_{org}$ values are found at sites within the core of the OMZ (200–1000 m), there is also major variability in $\%C_{org}$ (∼ 1–2 to 6–7 %) at sites of similar depth within the OMZ , especially in the more northern (Yokosuka) transects. This is in contrast to DO concentrations, which, apart from seasonal fluctuation at the upper OMZ boundary (Fig. 2), are comparatively constant, with season and at any given depth within the OMZ (as observed in repeat CTD profiles). There is also a large range of $\%C_{org}$ values in shelf sediments (i.e.

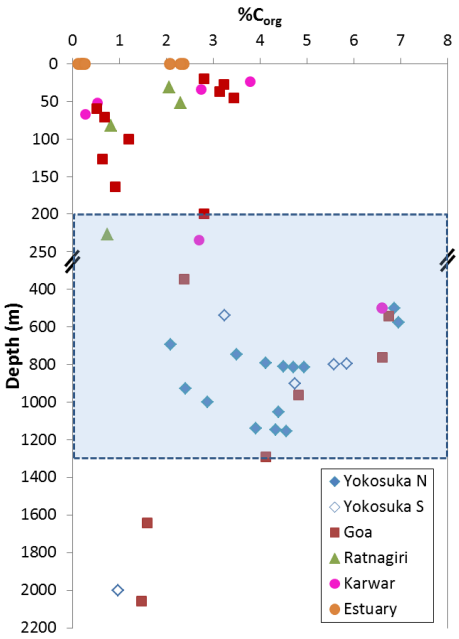

Figure 3. Organic carbon weight percentage ($\%C_{org}$) in surficial sediments (0–2 cm) from estuary, shelf and upper slope sites on the Indian margin of the Arabian Sea. Shaded area indicates approximate depth of permanent mid-depth OMZ (< ∼ 50 µM).

above the permanent OMZ), with values in shallow nearshore deposits notably reaching values (up to ∼ 4 %) similar to many observed on the slope (within the OMZ). Thus, the observed variability in sediment organic C content is not associated only with variations in DO. The cross-margin distributions are consistent with others reported previously for the Indian margin (e.g. Calvert et al., 1995), which also have shown maximal concentrations on the upper slope, but also, for some transects, major variability within the OMZ and, on occasion, maximal C_{org} values at or below the lower OMZ boundary.

By contrast, similar cross-margin transects from the Pakistan margin of the Arabian Sea (Cowie et al., 1999, 2009) showed less pronounced $\%C_{org}$ maxima on the upper slope (∼ 4 % max.) and these were found at the lower boundary of the OMZ (∼ 1000–1200 m), whereas DO was minimal at 300–400 m depth. However, within any given transect area on the Pakistan margin, $\%C_{org}$ values were remarkably constant at a given depth and DO value. Thus, the scatter observed within the OMZ on the Indian margin (Fig. 3 and Calvert et al., 1995) was not apparent off Pakistan. On the Oman margin, $\%C_{org}$ maxima are comparable to those observed in the present study (∼ 7–8 %) but, like the Pakistan margin, show elevated values at, or even well below, the lower OMZ boundary (e.g. Pedersen et al., 1992).

Station	Depth m	Lat. ° N	Long. ° E	DO * (µM)	%salt wt%	C_{org} wt%	TN wt%	C / N molar	$\delta^{13}C_{org}$ ‰	%(BALA +GABA)	%AA-TN	DI	Λ**	Median µm (∅)	%Clay	%Silt	%Sand
Upriver SPM***																	
Mandovi	nd	15.2650	74.0628	nd	nd	nd	nd	nd	−27.24 / −30.57	nd	nd	nd	nd	nd	nd	nd	nd
Zuari	nd	15.2667	74.1114	nd	nd	nd	nd	nd	−29.22 / −30.20	nd	nd	nd	nd	nd	nd	nd	nd
Estuary Sites																	
Zuari 1	< 3m	15.4110	73.9100	nd	4.0	2.36	0.19	14.4	−23.62	2.93	32.8	0.55	4.11	nd	nd	nd	nd
Zuari 3	< 3m	15.3675	73.9770	nd	0.6	0.21	0.02	13.0	−23.76	2.38	26.3	0.42	0.10	220.4 (2.18)	5.3	6.5	88.2
Zuari 5	< 3m	15.3032	74.0150	nd	0.5	0.19	0.02	11.1	−25.02	1.51	28.3	0.27	nd	334.8 (1.58)	7.0	9.3	83.8
Canal 6	< 3m	15.4350	73.9340	nd	2.4	2.08	0.18	13.6	−24.34	2.34	26.2	0.76	4.99	nd	nd	nd	nd
Canal 7	< 3m	15.4795	73.9500	nd	2.0	2.31	0.19	14.3	−25.17	2.49	32.1	0.58	1.81	14.81 (6.08)	26.0	50.0	24.0
Mandovi 9	< 3m	15.5364	73.9300	nd	1.1	0.19	0.02	13.8	−25.08	2.28	26.9	0.55	2.87	209.4 (2.26)	9.5	16.1	74.5
Mandovi 10	< 3m	15.5398	73.9600	nd	0.8	0.12	0.01	10.0	−23.59	3.30	26.7	−0.06	nd	nd	nd	nd	nd
Mandovi 11	< 3m	15.5068	73.9100	nd	1.0	0.27	0.02	13.3	−24.99	2.78	23.6	0.61	1.42	149.8 (2.74)	9.5	17.2	73.3
Yokosuka Transect N																	
1123 R10	500	17.5583	71.1891	0.5	15.4	6.87	0.81	9.9	−20.91	1.44	26.7	0.28	0.01	11.4 (6.45)	19.2	73.3	7.5
1123 R7	575	17.5555	71.1924	0.6	16.3	6.96	0.80	10.2	−20.95	1.63	23.7	0.14	0.00	12.61 (6.31)	18.5	71.1	10.4
1117 Y6	693	17.5365	71.1769	1.1	4.2	2.09	0.27	8.9	−20.34	1.71	21.6	−0.48	0.01	61.3 (4.03)	13.1	37.3	49.6
1117 Y8	746	17.5333	71.1753	1.3	5.9	3.51	0.44	9.3	−20.53	1.48	21.2	−0.12	0.00	55.4 (4.17)	9.7	42.2	48.1
1112 R8	793	17.5278	71.1733	1.4	6.4	4.13	0.47	10.2	−20.40	1.54	24.2	0.00	0.01	20.3(5.62)	14.9	49.9	35.2
1119 R4	812	17.5249	71.1704	2.8	7.5	4.50	0.51	10.3	−20.37	1.84	21.4	−0.16	0.01	29.2 (5.10)	13.6	48.8	37.6
1115 R9	813	17.5248	71.1696	2.3	5.7	4.94	0.58	9.9	−20.42	1.68	20.8	0.00	0.01	15.2 (6.04)	17.4	55.8	26.8
1112 R6	814	17.5252	71.1721	1.8	5.3	4.72	0.55	10.0	−20.22	1.96	22.5	0.05	0.00	16.6 (5.91)	16.8	55.8	27.4
1110 Y8	928	17.5430	71.1050	4.7	4.7	2.41	0.23	12.5	−19.79	2.11	22.7	−0.18	0.01	28.2 (5.15)	14.8	47.6	37.5
1116 Y3	1000	17.5304	71.1002	9.7	4.6	2.87	0.38	8.8	−20.51	1.99	22.6	−0.45	0.01	23.0 (5.44)	16.5	47.3	36.2
1110 R7	1139	17.5258	71.0850	22.7	6.3	3.92	0.46	10.0	−20.16	2.14	23.7	−0.10	0.01	13.2 (6.24)	18.6	67.1	14.3
1114 Y10	1145	17.5275	71.0806	21.2	5.7	4.34	0.55	9.1	−20.59	1.93	22.0	−0.02	0.01	11.7 (6.41)	20.8	63.5	15.7
1116 R10	1052	17.5297	71.0936	17.8	5.4	4.40	0.51	10.2	−20.14	1.92	22.0	−0.11	0.00	9.3 (6.74)	26.2	60.6	13.3
1114 Y3	1156	17.5254	71.0822	22.4	11.4	4.56	0.56	9.6	−20.32	1.90	22.4	0.02	0.00	8.4 (6.89)	28.6	60.5	10.9
Yokosuka Transect S																	
1109 R4	540	16.9804	71.9217	1.7	5.2	3.24	0.38	9.9	−20.38	2.60	21.5	0.13	0.01	38.2 (4.71)	14.8	41.2	44.0
1105 R6	795	16.9794	71.8683	1.1	7.2	5.84	0.67	10.2	−20.40	1.96	25.7	0.01	0.01	11.5 (6.44)	18.5	74.0	7.5
1101 Y4	798	16.9793	71.8678	2.2	10.3	5.57	0.63	10.3	−20.41	1.72	20.5	0.04	0.01	12.1 (6.37)	19.6	70.8	9.6
1100 Y2	900	16.9663	71.8518	4.7	6.6	4.75	0.57	9.7	−20.64	1.86	21.7	−0.01	0.01	12.0 (6.38)	21.0	64.7	14.3
1098 Y2	2000	16.7831	71.3356	108.6	7.2	0.98	0.15	7.4	−19.48	3.49	19.5	−0.77	0.01	8.9 (6.82)	28.0	63.1	8.9
Ratnagiri Transect																	
R2	31	16.7135	73.2079	48.7	4.9	2.07	0.22	11.2	−21.30	3.18	22.9	0.61	1.29	10.4 (6.59)	25.4	69.1	5.5
R4	52	16.6660	73.0512	66.0	9.5	2.31	0.27	9.9	−20.21	3.04	29.4	0.17	0.29	7.7 (7.03)	34.0	61.8	4.2
R6	82	16.5608	72.6289	78.4	3.5	0.82	0.08	11.5	−20.15	2.06	30.7	0.10	nd	102.8 (3.28)	21.3	21.7	57.0
R9	227	16.5383	72.2284	3.1	1.8	0.74	0.09	9.7	−19.84	1.54	15.5	−0.23	nd	199.4 (2.33)	11.6	19.8	68.7
Goa Transect																	
G4	20	15.5182	73.7036	78.7	9.5	2.80	0.32	10.2	−21.01	2.88	23.7	0.81	0.34	14.1 (6.15)	15.3	78.5	6.2
G5	28	15.5133	73.6518	85.4 (1.4)	9.6	3.23	0.31	12.0	−21.16	2.88	27.8	0.89	0.38	13.4 (6.23)	17.2	76.7	6.2
G6	37	15.4989	73.5827	88.2 (3.8)	9.2	3.13	0.30	12.0	−20.77	2.54	27.1	0.70	0.25	16.4 (5.93)	12.7	81.2	6.1
G7	46	15.4820	73.5150	90.2 (1.7)	7.8	3.45	0.36	11.2	−20.72	2.51	29.0	0.74	0.26	14.2 (6.14)	19.2	72.5	8.4
G8	60	73.4530	73.4020	31.7	1.4	0.52	0.08	7.9	−19.42	1.80	19.0	0.09	nd	176.0 (2.51)	8.8	13.9	77.3
G9	71	15.4277	73.2827	57.2	3.0	0.69	0.11	7.3	−19.93	1.58	17.8	−0.05	nd	176.1 (2.51)	8.4	12.8	78.8
G10	100	15.3685	73.1307	31.7	3.5	1.20	0.13	10.7	−20.65	1.21	21.1	0.12	nd	65.4 (3.94)	11.0	38.1	51.0
G11	127	15.3413	73.0035	22.6 (7.9)	2.2	0.64	0.07	10.4	−20.26	1.41	25.5	0.20	0.08	149.0 (2.75)	9.5	16.9	73.6
G12	164	15.2354	72.9810	76.8 (3.6)	2.4	0.91	0.10	10.3	−20.23	1.11	26.1	0.41	0.08	196.7 (2.35)	10.2	13.5	76.3
G12B	200	15.2253	72.9299	3.9	5.5	2.80	0.31	10.7	−20.89	1.75	27.7	0.46	0.06	48.8 (4.36)	18.2	34.5	47.2
G12C	346	15.3567	72.8241	3.8	9.4	2.39	0.26	10.5	−19.77	1.47	22.1	0.14	0.04	114.2 (3.13)	13.7	30.5	55.9
G12D	543	15.3063	72.8078	2.8	8.1	6.74	0.74	10.6	−20.24	2.46	31.6	0.29	0.03	6.8 (7.19)	32.5	63.2	4.3
G12E	760	15.2767	72.7644	5.7	5.4	6.60	0.66	11.7	−20.17	2.68	23.3	0.37	0.04	8.4 (6.89)	26.9	68.2	4.9
G13	960	15.2801	72.6742	24.4	6.6	4.82	0.51	11.1	−20.15	3.08	22.6	0.15	0.05	11.0 (6.50)	22.1	69.8	8.1
G13B	1290	15.2050	72.6107	37.7	9.7	4.12	0.43	11.3	−20.16	3.08	19.9	0.17	0.03	9.0 (6.79)	27.0	66.6	6.4
G14	1642	15.1170	72.4067	70.1	5.9	1.59	0.16	11.9	−19.80	5.15	18.9	−0.24	0.04	5.6 (7.49)	41.6	52.8	5.6
G15	2056	14.9968	71.0000	104.5	5.9	1.47	0.17	9.8	−19.85	5.52	16.7	−0.60	0.04	6.2 (7.33)	38.2	57.7	4.2
Karwar Transect																	
K2	24	14.4698	74.2416	29.1	8.1	3.79	0.34	12.8	−22.84	nd	nd	nd	1.71	17.6 (5.83)	13.4	73.7	12.9
K3	34	14.4679	74.1725	34.4	7.8	2.74	0.29	10.9	−20.97	1.75	28.6	0.39	nd	15.1 (6.05)	20.2	67.5	12.2
K5	52	14.3975	74.0004	72.6	2.0	0.53	0.05	11.5	−21.09	1.16	27.9	0.23	nd	83.1 (3.59)	11.6	26.2	62.2
K7	67	14.3195	73.7729	83.8	1.6	0.27	0.03	11.8	−21.22	1.04	31.8	0.03	nd	179.2 (2.48)	5.4	8.4	86.2
K8	235	14.1713	73.2607	2.5	4.7	2.70	0.29	10.9	−20.49	nd	nd	nd	nd	17.1 (5.87)	21.5	45.7	32.8
K9	500	14.1714	73.2316	4.4	7.1	6.60	0.69	11.1	−20.19	2.83	19.6	0.11	0.08	6.5 (7.27)	36.6	57.8	5.6

Site and sample compositional data. * DO values as recorded at time of sampling, intermonsoon (late monsoon); ** Λ = total lignin phenol yields in mg 100 mg^{-1} C_{org}; *** riverine suspended particulate material (SPM) collected in intermonsoon / late monsoon seasons. Median = median grain size; Clay, silt and sand are percentages by volume. Other parameters are as defined in the text.

3.2 Organic matter sources

The fate of terrigenous OM that enters estuaries and the coastal ocean is a subject of long-standing debate and current research (e.g. Hedges and Ertel, 1982; Hedges et al., 1997; Bianchi, 2012). For the present study, it is also important to establish the extent of terrigenous OM inputs in order to deconvolve observed cross-margin trends in C_{org} concentration. Distributions of parameters that serve as potentially diagnostic indices of terrigenous (versus autochthonous/marine) OM inputs are plotted in Fig. 4. These include stable C isotopic compositions ($\delta^{13}C_{org}$ [‰], Fig. 4a), total lignin phenol yields (Λ, mg 100 mg^{-1} C_{org}; Fig. 4b) and molar organic-C-to-total-N ratios ($[C/N]_a$, Fig. 4c).

Firstly, $\delta^{13}C_{org}$ values for sediments from the Zuari/Mandovi estuary sites ranged from −23.6 to −25.2 ‰ (Fig. 4a, Table 1). These compare to more negative values of −27.2 to −30.6 ‰ found in suspended particulate organic matter (SPOM) from upriver sites on the Zuari and Mandovi rivers (Table 1). These values in turn are in line with

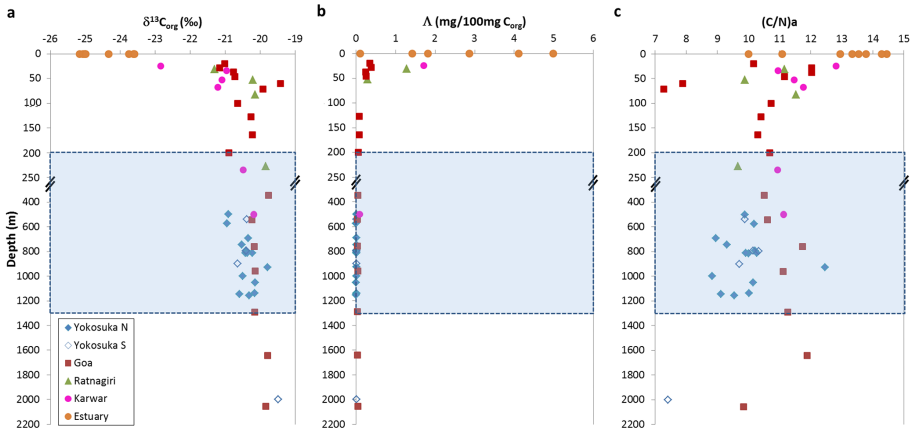

Figure 4. Plots against station depth (m) of **(a)** stable C isotopic composition ($\delta^{13}C_{org}$, ‰), **(b)** total lignin phenol yield (Λ, mg 100 mg^{-1} C_{org}) and **(c)** molar ratios of organic C to total N [(C / N)a], for surficial sediments from estuary, shelf and slope sites. Shaded area indicates approximate depth of permanent mid-depth OMZ ($< \sim 50$ µM).

previous studies which showed SPOM $\delta^{13}C_{org}$ values ranging from ~ -21 towards the mouths to ~ -32 ‰ towards the upstream ends of the estuaries, with values varying with season/discharge and tidal stage (Maya et al., 2011; Khodse and Bhosle, 2012; Kessarkar et al., 2003). Like these SPOM data, the results of the present study therefore indicate mixed OM inputs to sediments across the Zuari and Mandovi estuaries, with varying proportions of marine and terrigenous OM.

The $\delta^{13}C_{org}$ values of shelf sediments (Fig. 4a) become sharply heavier (more marine) even at the shallowest sites, with all but one site (K2, 24 m depth, Karwar transect) having values of −21.3 ‰ or heavier (with low- to mid-latitude planktonic signatures typically being in the range of ~ -18 to −22 ‰, Emerson and Hedges, 1988). There is some fluctuation in $\delta^{13}C_{org}$ values (−19.4 to −21.3 ‰) across the shelf (all three shelf transects) but relatively uniform values beyond the shelf break, with a possible trend towards slightly more positive values below 1300 m. These results indicate a strong and relatively uniform predominance of marine OM in the sediments at all sites except the shallowest and closest to shore. The more negative signature in the nearshore sediments on the Karwar transect may reflect a somewhat greater terrigenous input locally, possibly from the nearby Kali river (isotopic signature unknown). Finally, the lack of a clear trend in $\delta^{13}C_{org}$ across the slope and OMZ is in stark contrast to trends observed on the Pakistan margin (Cowie et al., 1999, 2009), where distinctly more negative $\delta^{13}C_{org}$ signatures within the OMZ were attributed to the imprint of chemosynthetic bacteria and/or to enhanced OM preservation. The lack of trend across the Indian margin may therefore be due to better ventilation and less pronounced hypoxia than off Pakistan (there is a progressive intensification of hypoxia from S to N), leading to absence of chemosynthetic processes and/or to less enhanced preservation of OM (see further discussion below).

Total lignin phenol yields (Fig. 4b) and molar C / N ratios (Fig. 4c) provide very similar indications to $\delta^{13}C_{org}$ signatures. Total C_{org}-normalised lignin phenol yields (Λ) are quite variable in the estuarine sediments, with a maximum of 5.4 mg 100 mg^{-1} C_{org}. However, there is a steep decrease offshore of the shallowest nearshore sites on all shelf transects. At all sites with depths greater than 100 m, on all transects, Λ values are ≤ 0.2 mg 100 mg^{-1} C_{org}. Carbon-to-nitrogen ratios are more ambiguous tracers of marine versus terrestrial OM inputs due the common and variable effects of diagenetic imprints (Meyers, 1994). However, the range of $(C/N)_a$ values in the estuarine sediments (10.0–14.5) again suggests varying proportions of marine and terrigenous OM (Fig. 4c). Moreover, lower, more typically marine values ($\sim$ 7–11) are found on the shelf, even in nearshore deposits, and at sites beyond the shelf break (although there is considerable scatter across the Yokosuka slope transects). There is also a possible trend towards lower values at greater depth (below the OMZ) due to lowering of C / N ratios with advanced degradation (Cowie et al., 1999, 2009).

A cross-plot of lignin phenol yields and $\delta^{13}C_{org}$ values (Fig. 5a) provides strongly coherent source indications. Sites from within the Mandovi/Zuari estuary system show variable lignin phenol yields and $\delta^{13}C_{org}$ values that fall within the range of values previously recorded for SPOM across the length of the estuary, but more positive (marine) than values recorded at upriver sites. These results confirm mixed marine and terrigenous OM inputs to the estuarine sediments, though it would appear that the lignin yield of terrigenous inputs is variable (i.e. there is not a uniform lignin yield for the terrigenous OM end-member). The two shallowest, nearshore sites on the Ratnagiri and Karwar transects show significant terrigenous OM inputs, based on both

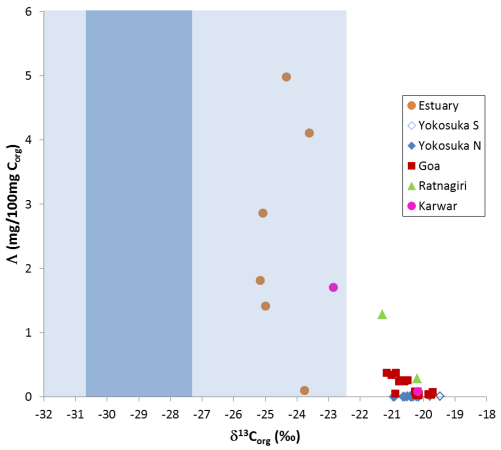

Figure 5. Plot for surficial sediments of total lignin phenol yield (Λ, mg 100 mg^{-1} C_{org}) against stable C isotopic composition ($\delta^{13}C_{org}$). Shaded areas indicate the range of $\delta^{13}C_{org}$ values found in upriver SPM samples (darker shading, this study) and across the Mandovi and Zuari estuaries (previous studies; see text).

parameters, but all sites further offshore on these transects, and all sites on the Goa and Yokosuka transects, have Λ values ≤ 0.54 mg 100 mg^{-1} C_{org} and $\delta^{13}C_{org}$ values of -21 ‰ or heavier. For illustrative purposes, taking a $\delta^{13}C_{org}$ value for the terrigenous OM end-member of -29 ‰ (average of values for upriver Mandovi–Zuari SPOM, Fig. 6a) and a value of ~ -19.5 ‰ for the marine OM end-member (approximate x-axis intercept at $\Lambda = 0$) gives an estimated marine OM contribution of 84 % or greater (up to 100 % on the slope) for all shelf and slope sites on all transects, other than the shallowest nearshore sites on the Ratnagiri and Karwar transects (81 and 65 %, respectively). Although the lignin and isotopic signatures of SPOM from other rivers along this section of the Indian coast are not established, they can be expected to be comparable as these rivers drain similar catchments with similar vegetation (also supported by very similar lignin phenol compositions for shelf sediments from all three transects; Table 1).

The apparent strong predominance of marine OM across both shelf and slope is characteristic of many margins (e.g. Burdige, 2005), even offshore of major river systems such as the Amazon (e.g. Keil et al., 1997). This, alongside significant contributions of marine OM to the Mandovi–Zuari estuarine sediments (41–57 %, by the same calculation as above), suggests that the large majority of terrigenous OM carried by these rivers (and others along this coast) is turned over close to source. As the large majority of OM in both riverine particulates and in coastal sediments typically is intimately attached to associated mineral surfaces (Hedges and Keil, 1995), the results indicate that terrigenous OM is efficiently re-mineralised and replaced by marine OM (Keil et al., 1997; Mayer et al., 1998; Burdige, 2005; Bianchi, 2012). We lack the surface area data for riverine particulates and sediments that would allow quantification of loss and/or replacement of terrigenous C as performed for the Amazon and other settings by Keil et al., 1997. However, the main conclusion to be drawn from the source indices is that, based on uniformly low lignin yields and narrow range of $\delta^{13}C_{org}$ values in shelf and slope sediments (Fig. 4), factors other than source are responsible for the large range of sediment OM content observed across this margin (Fig. 3).

3.3 Controls on OM distribution

Previous studies across the slope and OMZ on various margins of the Arabian Sea have concluded O_2 availability to be a primary control on sediment OM distribution (e.g. Paropkari et al., 1992, 1993; van der Weijden et al., 1998), based on correspondence between mid-slope C_{org} enrichment and the OMZ. Also, in studies of size-fractionated sediments from sites across the Pakistan margin OMZ, Keil and Cowie (1999) showed evidence of enhanced C_{org} loadings (relative to available surface area) at sites within the OMZ and close to its lower boundary. Moreover, differences in OM degradation state also have pointed to an O_2 effect, with enhanced preservation generally being linked to O_2 depletion within the OMZ (e.g. Schulte et al., 2000; Suthhof et al., 2000; Sinninghe Damste et al., 2002; Vandewiele et al., 2009). However, observed differences in preservation indices are slight compared to the several-fold range in $\%C_{org}$ values found below versus within the OMZ, and, moreover, other studies have found clear exceptions to any relationship between O_2 and either C_{org} content or OM quality. For example, Calvert et al. (1995), in a synthesis of results from the Indian margin, demonstrated multiple cases of C_{org}-enriched sediments at sites below the OMZ, and no clear cross-margin trends in hydrogen indices (a measure of hydrocarbon richness). Rather, they showed a strong positive correlation between $\%C_{org}$ and sediment grain size, expressed as %(Silt+Clay), for all slope sites falling in the depth range of roughly 200 m to $\sim$1500 m, with lower $\%C_{org}$ loadings found above and below these depths. These findings are evidence of a further important contributing factor, namely hydrodynamic processes. Thus, variability in C_{org} concentration within the 200–1500 m depth range was attributed to hydrodynamic equivalence of OM and fine sediment and/or to sorption of OM onto finer particles. Organic-poor sediments on the shelf were attributed to extensive reworking and/or winnowing of OM from carbonate sand deposits on the mid- and outer shelf, or to dilution of nearshore muds with organic-poor terrestrial clays. The paucity of OM at sites below 1500 m attributed not to increasing oxygen levels but to decreasing OM input to the sediment due to progressive offshore decrease in productivity and to greater decay within the increasing water column. In short, the interplay and relative importance of oxygen availability and hydrodynamic factors remains unclear and the subject of debate.

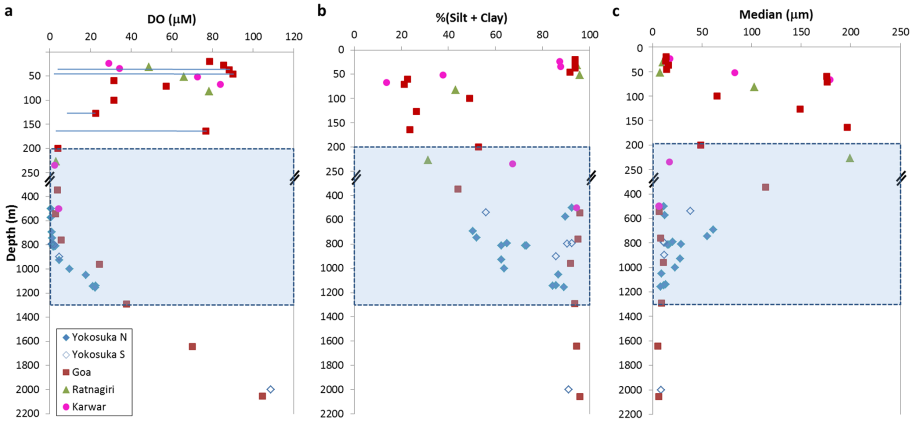

Figure 6. Plots against station depth (m) of **(a)** bottom-water dissolved oxygen concentration (DO, µM) at time of sampling, **(b)** percentage of silt and clay (by volume) in surficial sediments, and **(c)** median grain size (µm) in surficial sediments, from shelf and slope sites. DO concentrations were either measured directly from a submersible (Yokosuka transects) or in near-bottom bottle samples. All sediment samples and DO data for Goa, Ratnagiri and Karwar transect sites were collected during intermonsoon (normoxic) period. Horizontal lines for five Goa transect shelf sites indicate bottom-water DO values encountered during the late monsoon season (shelf hypoxia).

Bottom-water oxygen concentrations (Fig. 6a) exhibit the cross-margin trend expected for the intermonsoon (April/May) sampling period during which sediments from the Ratnagiri, Goa and Karwar transects were collected, thus showing oxygenated conditions on the shelf. However, as indicated in Fig. 2 and by bottom-water O_2 concentrations recorded at some of the Goa shelf stations during the late monsoon (Fig. 6a, October), the entire shelf experiences dramatic seasonal fluctuations in DO concentration, reaching $< \sim 10$ µM across the entire shelf during the monsoon, and 0 µM (sulfidic) at some inner shelf sites (Naqvi et al., 2000, 2006, 2009). Below a depth of ~ 200 m, values on the upper slope are comparatively stable, and reach a minimum (< 5 µM, but non-zero) between depths of ~ 200 m and 800 m. Below this, values progressively rise to ~ 100–110 µM at ~ 2000 m. Apparent differences between transects across the lower OMZ boundary (~ 800–1000 m; Fig. 6a) are most likely due to sampling method (direct on-bottom measurement on Yokosuka transects vs. near-bottom CTD casts on Goa transect). However, there may also be real spatial and/or temporal variation bottom-water DO levels across the lower OMZ boundary; (e.g. considerable fluctuation was observed at a single location over a 1-day benthic lander deployment, apparently related to tidal currents; H. Kitazato, personal observation, 2014). Problems with the accuracy of near-zero DO concentration measurements with many DO sensors have now been widely recognised (e.g. Revsbech et al., 2009). Thus, some values, especially those determined with CTD profiling, may be overestimates, but the presence of macrofauna in non-laminated sediments across the entire OMZ (e.g. Ingole et al., 2010), and the absence of sulfidic waters, are consistent with non-zero DO concentrations. This indicates better ventilation within the OMZ than off Pakistan, where sediments at the core of the OMZ are laminated and devoid of macrofauna (Cowie and Levin, 2009, and references therein).

Sediment grain size distributions show considerable cross-margin variation, both in %(Silt + Clay) (Fig. 6b) and in median grain size (Fig. 6c), as previously noted by Calvert et al. (1995). Sediments at all sites have non-normal distributions and are poorly sorted. Consistent with previous studies (e.g. Ramaswamy and Nair, 1989; Rao and Rao, 1995; Kessarkar et al., 2013), there is a narrow nearshore belt of muds (< 25 µm median, > 85 %(Silt+Clay)) at depths shallower than ~ 50 m, and a belt of coarser sediments extending to ~ 200–300 m (depending on transect). On the slope, sediments below ~ 400 m are generally finer (< 61 µm median), with an apparent gradual (slight) decrease with depth, and reaching 9–14 µm median at ~ 2000 m (Fig. 6c). These trends are paralleled in %(Silt + Clay) values (Fig. 6b), but this parameter more clearly shows that there is considerable variability in grain size distributions, especially for slope sediments from the Yokosuka transects.

A plot of $\%C_{org}$ against bottom-water DO concentration for shelf and slope surface sediments (Fig. 7a) does not provide definitive evidence for an O_2 availability effect on sediment OM content across the margin. Again, this mainly reflects the inclusion of shelf stations, for which appropriate DO values are uncertain. Considering the slope stations from the Goa and Yokosuka transects only (> 200 m; Fig. 7b), a wide range of $\%C_{org}$ is found for sites within the OMZ (~ 2–7 %), but there is a progressive decrease in $\%C_{org}$ values from a site near the lower OMZ boundary (~ 1000 m) to sites below, as bottom-water DO levels rise. The latter feature suggests that elevated C_{org} values within the OMZ, where they occur, may be associated with O_2 depletion. However, the wide range of $\%C_{org}$ amongst sites within the OMZ includes proximal sites; i.e. at equal depths as well as DO

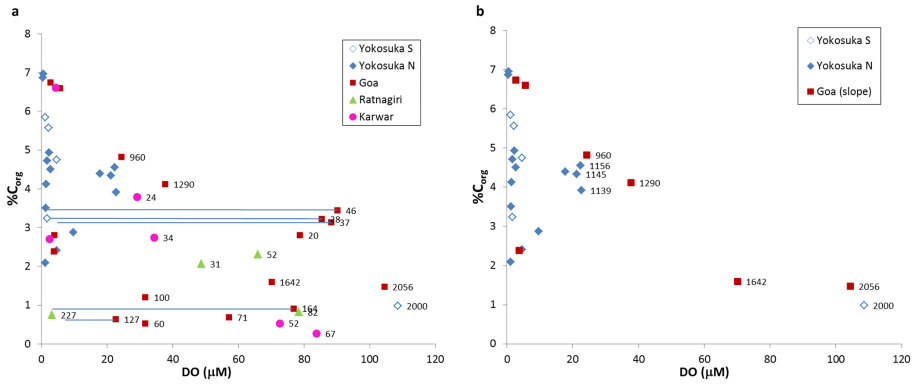

Figure 7. Plots of surface sediment organic C content (%C_{org}) against bottom-water dissolved oxygen concentration (DO, µM); **(a)** all sites, and **(b)** for slope sites (> 200 m) for the Goa and Yokosuka transects. DO concentrations were either measured directly from a submersible (Yokosuka transects) or in near-bottom bottle samples. All sediment samples and DO data for Goa, Ratnagiri and Karwar transect sites were collected during intermonsoon (normoxic) period. Horizontal lines for five Goa transect shelf sites indicate bottom-water DO values encountered during the monsoon season (shelf hypoxia). Data labels show station depths for shelf sites and slope sites near and below the lower OMZ boundary (> ∼ 1000 m).

concentrations. Further, %C_{org} values at some sites within the OMZ are as low as those found above or below (Fig. 3). Thus, while increasing DO levels may cause the decrease in %C_{org} below the OMZ, it is apparent that O_2 availability is not the universal or overriding control on C_{org} distributions across the slope. Its role on the shelf cannot be deduced from this analysis.

The relationship between %C_{org} and sediment grain size previously observed for other Indian margin sediments by Calvert et al. (1995) is also found for the present sample set, for both slope and shelf sediments. Specifically, %C_{org} values for sediments within the permanent OMZ (> 200 m to ∼ 1000 m) show a strong positive correlation with %(Silt + Clay), while values for sites from the shelf and below the OMZ (depths indicated by labels) show lower relative C_{org} loadings (Fig. 8a). Thus, while DO depletion may be responsible for C_{org} enrichments within the OMZ, hydrodynamic processes appear also to be an important factor, and can explain the wide range of %C_{org} values observed at sites with low and relatively uniform DO values within the core of the OMZ.

To test these inferences, we conducted a Pearson correlation analysis on the full data set (excluding station coordinates and metadata, and the estuary stations for which no DO data were available). Aside from expected (auto) correlations, such as between %C_{org} and %TN, and between % Sand, %Silt and %Clay, the strongest correlations were for %C_{org}, firstly with %Silt (+0.742), followed by that with %Sand (−0.719), and in turn by that with DO (−0.650). These are entirely consistent with the concept that interplay between hydrodynamic processes and O_2 availability controls sediment %C_{org} distribution across this margin.

Taking this forward as a hypothesis, we conducted sequential multiple regression analysis of %C_{org} against the applicable variables in Table 1. The results (as *R* values) indicate that %Silt (46 %) followed by DO (30 %) can account for 76 % of the variance in %C_{org} (with %Sand adding another 3 % and no other parameter responsible for more than 1 %). Furthermore, a similar analysis for slope sediments only (to eliminate uncertainty in DO values for shelf sediment) shows that variance in %C_{org} accounted for by %Silt and DO rose to 84 % (50 and 34 % respectively). No normalisation of data was conducted as the value ranges for C_{org}, silt and sand (percentages) were roughly similar to the range in DO values (∼ 0–100 µM). It should be noted that % Clay was a minor factor in all tests; this is consistent with findings of Keil and Cowie (1999) for size-fractionated sediments from the Pakistan margin, in which the major fractions of mass, OM and surface area were found in the silt fractions.

Therefore, hydrodynamic processes, expressed as %Silt, appear to explain more of the variance in %C_{org} across this margin than DO or any other measured parameter, and this is most pronounced on the slope, for sites within and below the OMZ. However, even this masks important detail. Further scrutiny reveals that for OMZ sites only (> 200–1000 m), %Silt and DO again account for a large fraction of the total variance (81 %), but %Silt is by far the dominant control (78 % vs. 3 %). The situation below the OMZ (> 1000 m) is reversed; the sample set is smaller but, while %Silt and DO account for 92 % of the variance in %C_{org}, DO becomes much more important than %Silt (79 % vs. 13 %).

Together, these results strongly indicate that progressively lower %C_{org} values below the OMZ, and enrichments within it, are due to enhanced OM preservation under O_2-depleted conditions, However, despite the enhanced preservation effect, the approximately fourfold variability in %C_{org} within the OMZ, where DO is almost invariant, is ultimately due to hydrodynamic effects, which become the overriding factor.

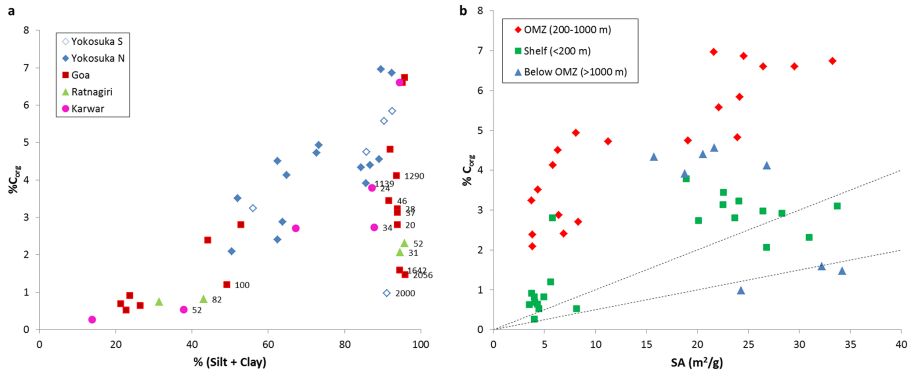

Figure 8. (a) A plot of organic C content (%C_{org}) against percentage (by volume) of silt and clay (%(Silt + Clay)) in surficial shelf and slope sediments. Marker labels show station depths for selected sites. **(b)** A plot of %C_{org} against estimated specific surface area (SA, $m^2\ g^{-1}$) for sediments from sites within, above and below the OMZ, here defined as sites at depths < 200, 200–1000 and > 1000 m, respectively. Dashed lines indicate the approximate 0.5–1.0 mg C m^{-2} range of organic C loadings commonly observed on normoxic margins (Hedges and Keil, 1995). Surface area values are estimated from a relationship observed for surface sediments from the Oman and Pakistan margins; SA = 251.42 $\times^{-0.761}$, where $\times$ is mean grain size (μM).

The C_{org} enrichment associated with O_2 depletion is more readily observed when C_{org} content is related to mineral surface area (e.g. Keil and Cowie, 1999; Arnarson and Keil, 2007). Using specific surface area values estimated from a relationship between measured surface area and mean grain size (μM) determined for sediments from the Oman and Pakistan margins (Cowie, unpublished data), all OMZ sediments showed %C_{org} values that are elevated relative to the ∼ 0.5–1.0 mg C_{org} m^{-2} range that is common to most normoxic shelf and upper slope sediments (Keil and Hedges, 1995) (Fig. 8b). Only sites at 1600+ m depth (i.e. with longest O_2 exposure times, well below the OMZ) showed C_{org} loadings below this range (as is characteristic of sediments on the continental rise and abyssal plain). The "excess" C_{org} found in sediments within the OMZ, for all grain sizes, indicates enhanced OM loadings over what would be attributable to hydrodynamic processes alone (Arnarson and Keil, 2007). Notably, the loadings for the OMZ sites are also elevated relative to those for sites with corresponding grain size distributions on the shelf. Thus, a possible explanation for the reduced C_{org} loadings in shelf sediments is seasonal exposure to O_2 that does not occur within the OMZ (see further discussion below).

The interplay between hydrodynamics and O_2 availability as controls is further illustrated and clarified through plotting %C_{org} against %Silt, and separating sites within and outside the OMZ (Fig. 9a). This confirms the importance of grain-size/hydrodynamics at low and relatively uniform DO values within the OMZ (here defined as < 10 μM), as reflected through the positive correlation between %C_{org} and %Silt ($r^2 = 0.78$) over a wide range of %C_{org} values. Although uncertainty remains over applicable DO values for shelf sites, a relationship is still seen with grain size at sites with higher DO levels (i.e. outside the OMZ), but C_{org} loadings are consistently lower. Further, there appears to be a progressive O_2 exposure effect; the extent to which %C_{org} values depart from the relationship with grain size observed within the OMZ in Fig. 9a increases with increasing bottom-water DO concentration (Fig. 9b). This is most evident for slope sediments. Shelf sediments adhere less well to this relationship, with sites having coarser sediments in particular appearing to have anomalously high %C_{org} values. However, this cannot be concluded with confidence due to uncertainty in DO values for shelf sites.

3.4 Organic matter preservation

Three amino acid parameters that provide indices of OM degradation state may offer further insight into the role that enhanced OM preservation in the absence of O_2 plays in causing observed cross-margin OM distributions. These are the percentages of total N in the form of amino acids (%AA-TN; Cowie and Hedges 1994; Fig. 10a), the percentages of total amino acids in the form of the non-protein amino acids β-alanine and γ-amino butyric acid (%(BALA + GABA); Cowie and Hedges 1994; Fig. 10b) and a Degradation Index based on multivariate analysis of whole amino acid suites across a sample set representing a full diagenetic spectrum (DI; Dauwe and Middelburg, 1998; Dauwe et al., 1999; Fig. 10c). Although these parameters may be sensitive at different stages of OM alteration (e.g. Cowie and Hedges, 1994), the clearest signal shown by all three parameters is that in both the Yokosuka and Goa transects, which extend below the OMZ, there is a consistent trend towards a greater degree of alteration that parallels the increase in DO levels from ∼ 1000 m near the base of the OMZ to the maximum sampling depth of 2056 m. Thus, the lower %C_{org} values observed below the OMZ appear to be linked to increasing extent of OM decay, as previously observed on the Pakistan

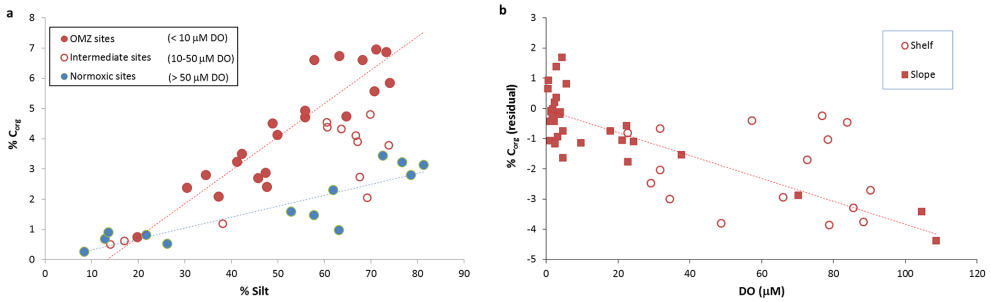

Figure 9. (a) A plot of organic C content (%C_{org}) against percentage by volume of silt (%Silt) for sediments from shelf and slope sites within the OMZ (closed blue circles; here defined by DO < 10 µM), and with normoxic (here defined by DO > 50 µM) and intermediate (DO = 10–50 µM) bottom-water oxygen concentrations (at the time of sampling, intermonsoon). Dashed lines indicate linear regression results for the OMZ and normoxic sites. **(b)** A plot of residual C_{org} values (departure from OMZ regression line in panel **(a)** for slope (> 200 m; red circles) and shelf (< 200 m; open circles) sites. Dashed line indicates linear regression results for all slope sites.

margin (Vandewiele et al., 2009), which can be linked to a progressive rise in O_2 exposure time (e.g. Hartnett et al., 1998; Hedges et al., 1999).

At sites within the OMZ, %AA-TN values vary without clear trend with depth or difference between transects (Fig. 10a). Values for %(BALA + GABA) and DI (Fig. 10b and c) similarly show no clear trend with depth within the OMZ. However, while the Yokosuka transect sites generally show lower %(BALA + GABA) values (less degraded), DI values are generally more negative (i.e. more degraded) than at corresponding sites on the Goa transect. Reasons for the slight contrasts between the three parameters are unclear, though it has previously been shown that %(BALA + GABA) values become most reliable as tracers of degradation state at late stages of alteration (Cowie and Hedges, 1994). Overall, results indicate no consistent trend in degradation state within the OMZ, and better OM preservation than at sites below the OMZ.

For the shelf sites, %(BALA + GABA) and DI values (Fig. 10b and c) show consistent differences between nearshore muds and mid-to-outer shelf relict sands, but provide directly contrasting indications of degradation state. Whereas the nearshore muds appear less degraded in terms of DI values (more positive, Fig. 10c), they appear more degraded in terms of %(BALA + GABA) values. Again, reasons for these discrepancies are unclear, but it is possible that the more terrigenous nearshore muds or the carbonate-rich sands were not amongst the sample types used in assessments of either parameter as indices of degradation state (Cowie and Hedges, 1994; Dauwe and Middelburg, 1998; Dauwe et al., 1999). Previous studies (e.g. Keil et al., 2000, and references therein) have indicated that preferential preservation of proteins and amino acids distinctively associated with specific phases, such as carbonate or silica tests or bacterial peptidoglycan, can influence sediment amino acid composition (and diagenetic indices) alongside the general process of diagenetic alteration. Although there are also differences in %AA-TN values (Fig. 10a) between the nearshore muds and some of the relict sands, there is more scatter and no consistent cross-shelf pattern. Overall, the three parameters suggest that OM at shelf sites is similar to or less degraded than at sites within the OMZ (e.g. when comparing muds at nearshore sites and on the slope). Thus, there are no consistent indications of more degraded OM at sites above the OMZ, as is seen at sites below the OMZ.

The central finding from the degradation indicators is therefore that the progressively more advanced OM degradation state at sites below the OMZ indicates that elevated C_{org} loadings within the OMZ (Figs. 8b and 9a) and the decrease in %C_{org} values below the OMZ (Fig. 3), are not due to decreasing OM delivery offshore as argued by Calvert et al. (1995). Rather, these trends are due to increasing decay with longer O_2 exposure, as concluded previously for several other margins, such as off Washington, Mexico and Pakistan (e.g. Hartnett et al., 1998; Hedges et al., 1999; Vandewiele et al., 2009).

On the other hand, there is a lack of consistent difference in degradation state between shelf and upper slope sediments from the OMZ, despite apparent difference in surface-area normalised C_{org} loadings (Fig. 8b). This indicates that the large cross-shelf differences in sediment OM content, which range from < 0.3%C_{org} in offshore sands to ∼ 4%C_{org} in nearshore muds, under near-identical (seasonally fluctuating) bottom-water redox conditions, are due more to physical effects (e.g. winnowing and redistribution) than to differences in OM preservation related to O_2 availability. The lack of a clear O_2 effect is perhaps to be expected at nearshore sites with short O_2 exposure times (Cowie and Hedges, 1992b; Hartnett et al., 1998), especially with the impact of seasonal hypoxia across the entire shelf.

Finally, down-core distributions of OM content and all compositional parameters over the upper 30–50 cm showed at most slight change (data not presented; Cowie, unpublished data). Cross-margin differences in sediment OM content and composition observed in surface sediments therefore are maintained down-core. This phenomenon, also observed

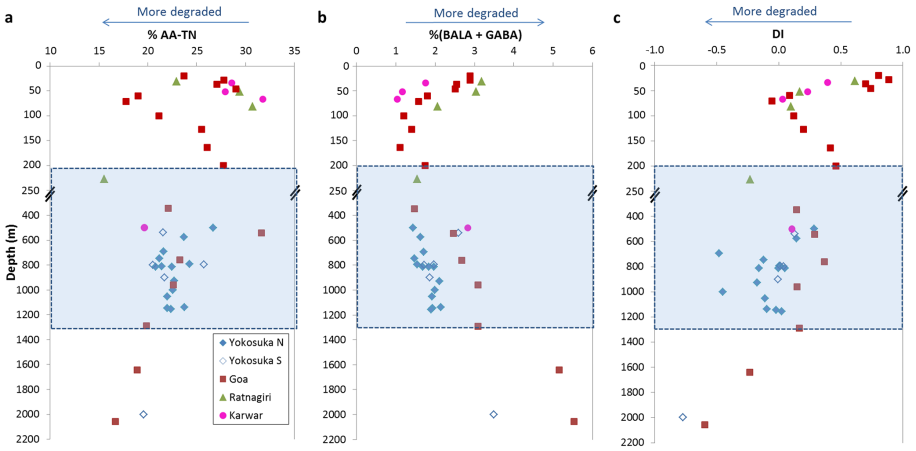

Figure 10. Plots against station depth (m) of **(a)** percentage of total N as hydrolysable amino acids (%AA-TN), **(b)** mole percentage of total hydrolysable amino acids in the form of β-alanine and γ-aminobutyric acid (%(BALA + GABA)) and **(c)** Degradation Index (DI) as per Dauwe and Middelburg (1998), Dauwe et al. (1999), for surficial shelf and slope sediments. Shaded area indicates the approximate depth of permanent mid-depth OMZ ($< \sim 50$ µM).

on the Pakistan margin, even at OMZ sites devoid of macrofauna and thus without masking of down-core profiles by bioturbation (Cowie et al., 1999, 2009), indicates that in situ OM alteration is generally limited. Thus, sediment OM contents and compositions are predominantly determined by processes occurring prior to deposition, within the water column or across the benthic interface.

4 Conclusions

In overview, the main findings of the present study are as follows:

- Source indices confirm mixed marine and terrigenous OM inputs to estuarine sediments, but little terrigenous OM outside the estuaries, indicating nearshore retention of terrigenous OM or, more likely, efficient remineralisation and replacement with autochthonous marine OM.
- Organic matter enrichment in upper-slope sediments is due to a combination of hydrodynamic processes (winnowing, cross-margin transport and sorting), enhanced preservation associated with low O_2 availability within the OMZ, and progressive decay of OM with increasing O_2 exposure below the OMZ.
- Major variability in sediment OM content across the shelf and within the OMZ is strongly linked to grain size distributions. Thus, while low O_2 exposure leads to OM enrichments within the OMZ, hydrodynamic processes are the overriding control on OM distribution, both across the shelf and within the OMZ.

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